

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Attorney Docket No: 37697-0062

Applicant(s): Edward W. MERRILL *et al.* Confirmation No.: 5033

Serial No.: 10/197,263 Examiner: Susan W. BERMAN

Filing Date: July 18, 2002 Group Art Unit: 1711

Title: RADIATION AND MELT TREATED ULTRA HIGH MOLECULAR WEIGHT POLYETHYLENE PROSTHETIC DEVICES

DECLARATION UNDER 37 C.F.R § 1.131

THIS DECLARATION IS TO BE MAINTAINED UNDER THE LIMITED ACCESS
PROVISIONS OF 37 CFR § 1.612; MPEP § 2309.03

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DECLARATION UNDER 37 C.F.R § 1.131

We, Edward W. Merrill, William H. Harris, Premnath Venugopalan, Murali Jasty, Charles R. Bragdon, and Daniel O. O'Connor, do hereby declare as follows:

1. We understand that the claims in the captioned application have been rejected over U. S. patent No. 6,281,264, which lists January 20, 1995 as the earliest filing date.
2. We submit this declaration, based on our personal knowledge to explain the process leading to the inventions disclosed in U. S. application Serial No. 10/197,263 that relate to orthopedic preformed materials and polymers, articles and the like that comprise polymers cross-linked by irradiation and heated to or above the melting point of the polymer, and methods of making same.
3. Wear of polyethylene and the incidence of osteolysis became known during mid-1980's. The realization was that the osteolysis was related to the formation of very small polyethylene particles through wear. In order to improve wear resistance of polyethylene and to prevent the formation of fine polyethylene particles, we carried out inventive activities and designed and carried out various experiments prior to January 20, 1995. All dates on the attached Exhibits have been masked out.

Cross-linking by Irradiation in a Molten State to lower crystallinity and Preserve the Entangled State

4. Prior to January 20, 1995, we developed several ideas to lower crystallinity and preserve the highly disordered entangled state of the ultra-high molecular weight polyethylene (UHMWPE) in order to solve the wear problem (see Exhibit 1). One embodiment that we developed was to cross-link the polyethylene in the molten state by use of irradiation so that the polyethylene could not revert readily to the chain folded state, which was preferred at the time. This embodiment is memorialized in item C of Exhibit 1. The process also is disclosed in U.S. Serial No. 08/600,744, filed February 13, 1996, and issued as U.S. Patent No. 5,879,400 (the '400 patent) (see, for example, Column 6, lines 55-67, and Example 1), U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 25, Example 1), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 33-34 , Example 1).

5. Prior to January 20, 1995, we conceived of various embodiments of the invention, that is irradiation of UHMWPE combined with melting, as described in item C of Premnath Venugopalan's note (see Exhibit 1). At the time, we believed that a prosthesis formed out of UHMWPE bar stock that had been heated above the melting point and irradiated (in air or an inert environment) in that molten state (see item c), or had been irradiated and then heated above the melting point, would form cross-links (see item b). The increased mobility of the molecules in the molten state allows the free radicals to combine with each other and form cross-links, as opposed to remaining in a trapped state.

6. Prior to January 20, 1995, we continued conducting melt-irradiation (MIR) experiments at Mr. Kenneth Wright's laboratory (the High Voltage Research Laboratory (HVRL), located in building N-10 of M.I.T. at 155 Massachusetts Avenue, Cambridge, MA 02139. Mr. Kenneth Wright was responsible for the day-to-day operation and management of the radiation applications activities of the HVRL, including scheduling, operation, maintenance of equipment and research with the Van de Graaff

accelerators). Six UHMWPE samples were irradiated at 1.0, 2.5, 5, 10, 20 and 50 Mrads by Mr. Ken Wright. The samples were heated to melt and irradiated while in a molten state. Subsequently, MIR experiments using solid bars in sealed containers (sealed glass vials) were done at Mr. Wright's laboratory. Copies of Mr. Wright's laboratory logbook page numbers 122-123 and 126-127 containing the record of MIR work done are attached as Exhibit 2. A copy of the corresponding page 10 of lab book no. 2 is attached as Exhibit 3.

7. Also, prior to January 20, 1995, we conducted a thermal analysis of the irradiated UHMWPE specimens, as described in paragraph 9, by use of DSC. This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity.

Six polymer samples, as described in paragraph 9, also were irradiated in sealed pans for crystallinity analysis. The samples were heated to melt and irradiated while in a molten state. A copy of Premnath Venugopalan's laboratory note book page numbers 8-9 is attached as Exhibit 3 (see Expt 1 and Expt 2). Thus, prior to January 20, 1995, we have practiced the process of heating polyethylene to a temperature at or above the melting point of polyethylene and irradiating the polyethylene in a molten state. The DSC testing on the polyethylene samples that were irradiated in a molten state was conducted. Crystallinity levels had dropped to 37.77% (printed as 37.8%) for the sample given a 20 Mrad radiation dose. Copies of the corresponding DSC data sheets are attached as Exhibit 4 (marked as 'data-6'). Crystallinity data from unirradiated GUR415 bar stock was used as control. Irradiation dose (20 Mrad), temperature (125.51, printed as 125.5) and crystallinity data (37.77%, printed as 37.8%) from this work are presented in a patent application that became the '400 patent (see, for example, Table 1 on column 9 of the '400 patent), in the '313 application (see, for example, Table 1, page 27), and the '638 application (see, for example, Table 1, page 35).

8. Other tests on melt-irradiated polyethylene, for example, Electron Spin Resonance (ESR), were conducted to determine residual free radicals. Swell Ratios to assess degree of cross-linking also were determined, prior to January 20, 1995, by submerging polyethylene in DecalinTM at 150°C for dissolution of polymeric chains.

ESR results indicated no detectable free radicals in melt-irradiated polyethylene, whereas the control polyethylene that was irradiated at room temperature without concurrent or subsequent melting showed the presence of free radicals. The absence of free radicals in the melt-irradiated polyethylene indicates that any further oxidative degradation would be avoided, and thus the material was suitable for use in medical prostheses. See Exhibit 5 for ESR spectra from an experiment conducted prior to January 20, 1995. The ESR spectra show samples irradiated at room temperature contain free radicals; whereas, the samples irradiated at 175°C do not have any detectable free radicals.

Swell Ratios indicated that the melt-irradiated polyethylene was highly crosslinked and did not allow dissolution of polymeric chains, while unirradiated polyethylene dissolved completely, which signifies lack of cross-linking in the unirradiated polyethylene. See Exhibit 6 for swell test results of an experiment conducted prior to January 20, 1995. Swell test data shows control specimens dissolve completely within 24 hours in DecalinTM at 150°C.

9. The above testing confirmed that we had invented, among other things, (1) methods of making an improved prostheses by combining melting and irradiating to cross-link UHMWPE, and (2) improved prostheses that were the result of these processes. These prostheses are wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

Cross-linking by irradiation at room temperature and subsequent melting

10. Prior to January 20, 1995, we also developed another embodiment to preserve the highly disordered entangled state of the UHMWPE in order to solve the

wear problem (see item b of Exhibit 1). The embodiment involved cross-linking the polyethylene in at room temperature ('cold irradiation') by irradiation and subsequent melting. The process is referred to as Cold-irradiation and Subsequent Melting or "CISM" and is disclosed in U.S. Serial No. 08/726,313 (the '313 application, filed October 2, 1996) (see, for example, page 39, Example 8), and U.S. Serial No. 08/798,638 (the '638 application, filed February 11, 1997) (see, for example, pages 47-48, Example 8).

11. According to this embodiment, UHMWPE is irradiated at room temperature to cross-link and subsequently the irradiated UHMWPE is heated above the melting point of about 135°C and then cooled. This process subsequently referred to as cold irradiation and subsequent melting or "CISM", meaning irradiation of UHMWPE at about room temperature and then heating the irradiated UHMWPE above the melting point and resolidifying.

12. Prior to January 20, 1995, we had a number of UHMWPE specimens irradiated at room temperature at Mr. Kenneth Wright's laboratory. A copy of Mr. Wright's laboratory logbook pages number 120-121 containing a log of irradiation work done prior to January 20, 1995 is attached as Exhibit 2. The experiment (Marked as Irradiation Experiment 1) and the process including radiation doses used are recorded in lab note book no. 2, page no. 8. A copy of the laboratory note book page number 8, which is attached as Exhibit 3.

13. Prior to January 20, 1995, we conducted a thermal analysis of the room-temperature irradiated UHMWPE specimens, as described in paragraph 11, by use of a testing method called differential scanning calorimetry ("DSC"). This DSC method is used to determine melting and crystallization temperatures as well as the energy input required to melt and energy output generated during crystallization. The energy required to melt is then used to quantify the degree of crystallinity. This DSC method generally has two heating-cooling cycles during which the energy input and output is measured. The cycles include of heating the specimen to a temperature above its melting point, cooling down to room temperature, and heating again to a temperature

above its melting point. The first cycle of this DSC method, involved heating and cooling, was applied to the room temperature irradiated UHMWPE test specimens, as described in paragraph 10 above. Therefore, we practiced the "CISM" process prior to January 20, 1995. The DSC test results indicated that the crystallinity levels decreased from approximately 54.71% present in the starting material to as low as 41.69% when irradiated at 20 Mrad. A copy of that data sheet is attached as Exhibit 4 (see sheet marked as 'data-4') and the corresponding DSC data sheet is attached as Exhibit 4. This reduced crystallinity confirmed our view that the "CISM" method also would improve the structure and wear resistance of the UHMWPE by decreasing the content of chain-folded crystalline lamellae, which otherwise would lead to fibril formation.

The above testing confirmed that we had developed (1) methods of making improved prostheses using the CISM method to cross-link UHMWPE, and (2) improved prostheses that were the result of the process. These prostheses would not be a source of the fine particles that would result in bone resorption as was the case with the prior art UHMWPE prosthesis. Subsequent testing also confirmed that the elimination of free radicals was provided by this method. Thus, prior to January 20, 1995, we conceived and reduced to practice the CISM invention, that is irradiation of UHMWPE at room temperature and subsequent melting, as described in item b of Exhibit 1.

14. The above testing confirmed that we had invented, among other things, (1) methods of making an improved medical implant having bearing surface comprising a solid polyethylene by irradiating to cross-link UHMWPE and subsequent melting, and (2) improved medical implants. This medical implant would be wear resistant and thus would not be a source of the fine particles that would result in bone resorption, as was the case with the prior art conventional UHMWPE prosthesis.

We hereby declare that all statements made herein of our own knowledge are true, and that all statements made on information and belief are believed to be true; and further, that these statements are made with the knowledge that willful false statements, and the like so made, are punishable by fine or imprisonment, or both,

under Section 1001, Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date

Edward W. Merrill

Date

William H. Harris

Date

Premnath Venugopalan

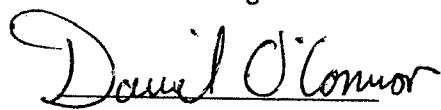
Date

Murali Jasty

Date

Charles R. Bragdon

Date


Daniel O'Connor

Daniel O. O'Connor

EXHIBIT - 1

BULK CROSS-LINKING FOR IMPROVED UPE PROPERTIES

↳ starting

BASIC MOTIVATION :-

It is clear that as mol. wt. of PE increases, it's abrasion resistance increases. Further as hypothesized by Prof. Merrill, the increase in entanglements should reduce wear. ~~Both ways~~ ^{there seems to be} an effort at increasing the resistance of PE chains to ~~being~~ pulled out of the bulk.

Hence, the following treatments ~~are~~ are being considered as ways to increase the resistance faced by PE chains against being pulled out:

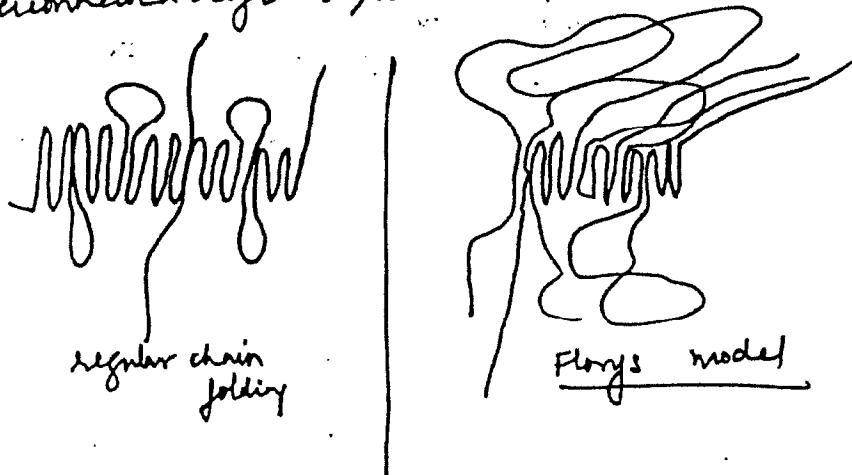
(a) Heat and rapid cooling: Heat the polymer to a completely disordered ~~state~~, highly entangled state and then suddenly cool it ~~down~~ in order to trap it in that state.

This may be possible with 10 μ thick films dipped into liquid N₂ but it is not possible for larger specimens (Researchers have used several 100 to 100,000 μ /min). Further there are problems of differential crystallization at different positions and problem of strain concentrations.

(b) Crosslink as solid, melt, recrystallize: Irradiating the polymer as a solid will mean ~~crosslinking~~ ^{crosslinker} at the crystalline zones but higher crosslinking in the amorphous zones (more mobile chains can ~~jump~~ move to connect at different places). Melting & recrystallizing these will probably again lead to the original crystal structure ~~though with reduced crystallinity~~ and selective segregation of crosslinks into the amorphous regions. This is expected to be more wear resistant since molecules in the tie regions may be interconnected & crosslinked. Promises to be useful if (a) inter-crystalline region slip is

important during wear (b) if loss in hardness is not crucial.

(c) Crosslink as melt, recrystallize: More reduction in crystallinity expected with uniform crosslinking (much more than in x-linking of the solid). More likely that chain-folding in the Flory sense, where ~~chains do not~~ ^{will occur} do instead of one chain folding repeatedly, ~~many chains~~ many chains will fold in a given region. Here ~~the~~ the amorphous region will have more interconnected regions, x-link points & longer loops.



(d) Crosslink the solid:

~~the~~ Hardness of original VPE is retained and hopefully there will be ~~more~~ ^{more} selective crosslinking in the amorphous regions.

Questions/Concerns :

① Degradation vs. Crosslinking

Mol wt ↓
Xstallinity ↑
Wear ↑
Free radicals
(long term existence)

Extent %

② Crosslinking vs. Crystallinity

↓
decreases as
xlinking ↑ (if uncrosslinked)

③ Crosslinking vs. Crystal structure

Ideas :

① Crosslinking by irradiation of
Hylamer after it has been peeled
and no recrystallization. \Rightarrow highest crystallinity
+ Crosslinking.

② Study crosslinking in HDPE instead to see
extent of crosslinking, degradation etc.

IRRADIATED SPECIMENS
FROM ZIMMER

$$\frac{1 \text{ Mrad}}{10^{-7} \text{ erg/g}} = 10^8 \text{ erg/g}$$

$$10^{-2} \text{ Gray} = 1 \text{ rad}$$

$$\frac{1 \text{ Gray}}{100 \text{ rad}} = \frac{1 \text{ J/kg}}{10^3 \text{ g}} = 10^7 \text{ erg/g}$$

Data 2

DSC RESULTS:

Effect of freezer-milling
and Effect of crosslinking by irradiation

Sample	T_{m1} ($^{\circ}$ C)	T_c ($^{\circ}$ C)	T_{m2} ($^{\circ}$ C)	% Cryst. 1	% Cryst. 2	Difference in Crystallinity	Ang. Lattice Distances 1	Ang. Lattice Distances 2
GUR 415 - CONTROL	135.83	122.00	127.52	62.91	46.42	16.49	2.91×10^{-6}	1.51×10^{-6}
(M34)							-0.30	0.653×10^{-6}
GUR 415 - FREEZER- MILLED - 10 min.	121.86	154.11	104.47	0.28	0.57	Again low order after irradiation?	1.15×10^{-6}	
BAR - CONTROL	127.39	121.71	126.57	52.92	46.37	6.55	1.52×10^{-6}	1.44×10^{-6}
						Nearly complete crystallization		
BAR - 10 M Rad	130.53	123.95	119.05	54.62	45.29	B-73	1.84×10^{-6}	1.02×10^{-6}
BAR - 20 M Rad	131.05	129.48	119.78	54.95	41.69	13.26	2.05×10^{-6}	1.05×10^{-6}

EXHIBIT - 2

1.45

COOP COMPUTATION BOOK

NAME	NUMBER
KEN WRIGHT	1

Course F-13-a.m.

Used from..... to.....

HARVARD COOPERATIVE SOCIETY
1400 MASS. AVE., CAMBRIDGE, MASS. 02138

TECH. COOP
84 MASS. AVE. CAMBRIDGE, MASS. 02138

Polyethylene fibers George Arinez 1-2 2.5 94. 303 ~~8.0~~ 340 sec 7.1 1.3 2×10^6 ~~HTT~~
 mounted on Al Port Number 56 - 37 13 93. - - 10^6
 plats ~0 and my 3-2265 1-2 - - - - - 10^6
 .2 $1/4$ hr - - 74 30. 1.12W 340 sec - 2×10^6 ~~HTT~~

Uchu Mukai 1-2 2.6 68 ~~27~~ - 75 - 1.3 2×10^6 ~~HTT~~
 1.5 hrs 3-6478 1-2 2.56 76 30 - - 2×10^6 ~~HTT~~

" Polyethylene fiber George Arinez 1,1⁰ 2.52 76 30 - 225 sec - 2×10^6 ~~HTT~~
 mounted on Al
 1.5 hrs ¹ Block - - - - 1.95 - - 10^6 ~~HTT~~

3 mm in Ambuj.
 bucket 1-16 2.5 17. 6.8 11 320 1.3 5×10^6 ~~HTT~~
 5-16 - 34 13.6 - 250 - 10^6
 9-16 - - - - - 790 - - 10^6
 13-16 - - - - - 120 - - 10^6 ~~HTT~~

Teflon in narrow Bertrand Schmitt 1-5 2.5 34 13.6 - 165 - 10^6 ~~HTT~~
 solns. H₂O, MVR, Acetone (Merrill)
 3-5 - - - - - 120 - - 10^6
 6-8 - - - - - - - - 10^6 ~~HTT~~

Ethylene Vinyl Ambuj.
 Alcohol 1-6 - - - - 160 - 10^6 ~~HTT~~
 2-6 - - - - - - - - 10^6 ~~HTT~~
 3-6 - - - - - - - - 10^6 ~~HTT~~
 4-6 - - - - - 90 - - 10^6 ~~HTT~~
 5-6 - - - - - - - - 10^6 ~~HTT~~
 6 - - - - - - - - 10^6 ~~HTT~~

Al poly polyethylene *
 Polyethylene on glass slides * 1-6² - - - - 185 1.3 10^6 ~~HTT~~
 1-82⁰ - - - - - - - - 10^6 ~~HTT~~
 1-5² - 60 20.4 - - - 1.5×10^6 ~~HTT~~
 1-10² - 35 15.2 - 165 - 1.5×10^6 ~~HTT~~
 1-85⁰ - 43 17 - 120 - 1.2×10^6 ~~HTT~~
 1-3² - - - - - 110 - - 10^6 ~~HTT~~
 1-2² - - - - - - - - 10^6 ~~HTT~~
 1-7² - - - - - 75 - - 10^6 ~~HTT~~ $\frac{1}{2} \times 10^6$ ~~HTT~~

Teflon in PEO Bertrand Schmitt 1-7 - 35. 13.7 11 120 - 10^6 ~~HTT~~
 in small cloth no cloth
 ~1" dia. & >4" high walls

Polymerized in Mervill
 polymerized in glass under MVR
 expansion & MVR 1-9 2.5 41 15. 1.1 13. 1.3 1.25×10^6 ~~HTT~~
 Schmitt 1-2² - - - - - - - - 10^6 ~~HTT~~
 1-2² - - - - - - - - 10^6 ~~HTT~~

4411 $\Sigma 15 \times 10^6$ with overlays estimate $\Sigma 40 \times 10^6$ (6 sheets $\approx 1/16$ sheet)

Turned over

4411 $\Sigma 15 \times 10^6$ with overlays

overlays, for

$\Sigma 95 \times 10^6$

$\Sigma 75 \times 10^6$

$\Sigma 7.5 \times 10^6$ (4 overlays ≈ 3 mts)

$\Sigma 15 \times 10^6$ Block turned over

$\Sigma 15 \times 10^6$ Turned over

$\Sigma 10 \times 10^6$

$\Sigma 2 \times 10^6$

$\Sigma 4 \times 10^6$

$\Sigma 8 \times 10^6$

$\Sigma 5 \times 10^6$ Petri dishes 2-5 overlays

$\Sigma 7 \times 10^6$

$\Sigma 5 \times 10^6$ 2 overlays

$\Sigma 2 \times 10^6$ 2 overlays

$\Sigma 4 \times 10^6$

$\Sigma 8 \times 10^6$

$\Sigma 12 \times 10^6$

$\Sigma 16 \times 10^6$

$\Sigma 2 \times 10^7$

$\Sigma 2.2 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 10^7$

$\Sigma 2 \times 10^7$

$\Sigma 5 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 20 \times 10^6$ 2 overlays

$\Sigma 5 \times 10^6$

$\Sigma 5 \times 10^6$ 2 overlays

Marill 10 25 41 15 61 75 1.3 1.25810

Bertrand 1-2 2.5 3.9, - - - 90 - - - - - $= 1.625 \times 10^6$ ft

1120 collagen Perc 1-9} 25 62 24.11 430 13 2x^d
Collagen in millipermol/liter 1-6}

TSO Litter Ligur N.2

PMMA	East Williams	1	2.5	2.0	8.1	1.11	40	3.2	2.5 x 10 ⁵
v4" dia discs 1/2" thick		2	-	2.6	10.2	-	-	+ 3.0 x 10 ⁵	
		3.5	-	2.6	-	-	-	-	-
		6-8	-	-	-	-	-	-	-
		9-10	-	1.7	6.8	-	58	-	2.0 x 10 ⁵
3/8" thick		11	2.0	3.3	10.2	-	40	-	3.0 x 10 ⁵
		12-15	-	3.9	11.9	-	40	-	3.0 x 10 ⁵

1-3 Counter Schmitt	1-18	2.5	39	15	1.1	400	1.13	1.20x10 ⁶
4-9 chs of PEO ⁺ different	1-13	?	?	?	?	?	?	3.28x10 ⁶
concentrations	2-8	?	?	?	?	200	?	5.58x10 ⁶

Thin Alms Polychrothra 1-3 - 30 12 - 100 1.3 10^6
 Mymica Mysleth 4-6 - - - - -
 3-2108, Km 35-332 - 7.25×10^{11}

Small (0.5 cm) <i>Premnath Venegorallu</i> (dia) cm	2.5	39	15	14	7.5	4.3	1.35 x 10 ⁶
2-3	-	-	-	-	-	-	-
3-4	-	-	-	-	-	-	-
4-5	52	20	-	-	-	-	111
5-6	63	39	17	17	-	-	271.6 + 111
6	-	-	-	-	-	-	21.111
6	-	-	-	-	-	-	111

Slush Tufts. M.R. Med. Center 1.4 2.5 33 13.1 -430 1.5 10⁶ 11

Various strips Schmit $\frac{1}{6}$ $\frac{38}{6}$ $\frac{15}{6}$ $\frac{125}{6}$ $\frac{125 \times 10^6}{6}$

No overlay (different liquid overlay)

$\Sigma 2.5 \times 10^6$

Glycerol overlay

$\Sigma 1.6$ over central area

No Pb.

2 overlays

$\Sigma 2.5 \times 10^6$ * Human over

$\Sigma 5 \times 10^6$

$\Sigma 2.5 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 1.0$

$\Sigma 2 \times 10^7$

$\Sigma 3 \times 10^7$

$\Sigma 4 \times 10^7$

$\Sigma 5 \times 10^7$

2 overlays

$\Sigma 5 \times 10^6$

$\Sigma 5 \times 10^6$ + 1.0 may be slightly less than $\Sigma 5 \times 10^6$

$\Sigma 4.5 \times 10^6$

$\Sigma 5 \times 10^6$

Polyethylene + Glycerin Pyrolyzed Acetone, water	Schmitt	1-2 26 50 20 1.1	6.3×10^6
PIE ^o in Petri dish Stephe...	Stephane	1-10 26 30 12 1.1 2.00	1.3×10^6
	Prof. Cimbra		
Stephani Lopina		1-10 ~ 60 24 - 340	$- 2 \times 10^6$
3-7115		1-20 - - - 440	$- -$
354-7489			
Buck-wheat + dates	Cat Cooke	1 26 60 24 1.1 140 2 - - - - 280 3,4 - - - -	1.3×10^6 $- - - -$
1mmx6" (1-1)	Ken Breckland-8	2,1 176 6.8 1.0 140	3.2×10^5
(Fractile)	B.U.	7-12 ~ 17.5 6.0 - -	
17-32,	Dept of Astronomy	725 Comm. Ave 13-32	
Cubes + other shapes		02215 53-42	1.40
		353-2625 -	1.40
			8.5
PTFE + Polyethylene		1-3 ~ 37 15 1.1 140	1.3×10^6
PRO*			
PRO in Petri dish see above	Prof. Cimbra	1-20 ~ 30 12. 6.1 480 1-15 - 60 24 - 360	1.3×10^6 $- 2 \times 10^6$
Polyethylene over hot plate	Premnath Varangopal-8	1-4 2.8 70 30. . 85 1-3 - - - - - 1-2 - - - - - 1 - - - - - - - - - -	$- 2.5 \times 10^6$ $- - -$ $- - -$ $- - -$ $- - -$
See above	Stephani Lopina	1-15 2,6 30 12 1.1 355	1.3×10^6
Polyethylene 1st hot plate	Premnath Varangopal-8	2,6 37.0 15 - 135 1-3,5-7 * 52 1-2,5-6 2.8+ 52 24 - 105 1,5 - - - - - 1,1 - - - - -	1.3×10^6 $- 1.83 \times 10^6$ $- 2 \times 10^6$ $- - -$ $- - -$
PIE ^o Soln PTFE Schmidt	Schmitt	1-2 ^o } 2,6 37.5 15 - 165	$1.3 \times 1.25 \times 10^6$
Polyethylene * small bends	Premnath	1-4,6 } 2.6 37.5 15 - 165	
1-6*		1-4,1-5 } - - - - -	
		1-2,6 } - - - - -	
		1-9,1-4 } - - - - -	
		1-3,1-4 } - - - - -	
		1-3,1-3 } 2.75 47 20 - -	
		1-3,1-2 } - - - - -	
180 L Ni		1,1* - 24 ~ 100	$- 1.06 \times 10^6$ $- 1.4 \times 10^5$

2nd day

$\Sigma 2 \times 10^6$

Tuned over for 2nd run

1 discharged

Patent 17 in glass chamber

$\Sigma 2 \times 10^6$

$\Sigma 10^7$

$\Sigma 2 \times 10^7$

$\Sigma 5 \times 10^7$

$\Sigma 5 \times 10^7$

$\Sigma 2 \times 10^6$

$\Sigma 2 \times 10^6$ 1st run hot plate jammed before insulation - re-entered and passed through

$\Sigma 9.8 \times 10^6$

$\Sigma 19.8 \times 10^6$

$\Sigma 29.8 \times 10^6$

$\Sigma 49.8 \times 10^6$

$\Sigma 2.5 \times 10^6$

$\Sigma 5.75 \times 10^6$

$\Sigma 5 \times 10^6$

$\Sigma 10^6$

$\Sigma 2 \times 10^6$

$\Sigma 5 \times 10^6$

EXHIBIT - 3

Student's Name

Date

8

Subject

Instructor's Name

Irradiation
Studies

→ e- beam
at HVRL, MIT

Kenneth A. Wright.

Student's Name

Date

Subject

Instructor's Name

8

Expt

① \rightarrow Irradiation of solid polymer (UPE) from bar stock

Set 1

Set 2

12 samples
of thickness of a
few millimeters kept
between two slides

6 samples in
DSC pan

RT

1.0 MRad (2 each)
2.5 MRad
5.0 MRad
10.0 MRad
20.0 MRad
50.0 MRad

RT

1.0 M Rad
2.5 " "
5.0 " "
10.0 " "
20.0 " "
50.0 " "

This was for
studies under
polarizing
microscope
at MGII

DSC Runs done
for results in
the file (# 3)

Result \rightarrow all

showed
Spherulites

On heating & cooling
under microscope

EXPT.

(2) Irradiation of barstok while a mett.

9 rad / 175°C / Air / No follow up / PANC

FHT

6 Samples \rightarrow 1.0, 2.5, 5, 10, 20, 50 Mrads.at temp. \geq 150°C

range (155 to 180°C approx.)

Heating \rightarrow Sample heated ~~approx 1 min~~
intermittentlyHeated \rightarrow 1.0 Mrad \rightarrow Heated \rightarrow 2.5 Mrad10 Mrad \leftarrow Heated \leftarrow 5.0 Mrad \leftarrow heatedHeated \rightarrow 20 Mrad \rightarrow Heated \rightarrow 35 MradHeated
50 Mrad

Samples placed on a heated Al-plate (fork)

Analysis \rightarrow In file #3.DSC trivia :Dosemg

9.732

11.433

9.540

9.061

10.133

11.638

There was some confusion because the heating ~~overshot~~ the marks on the spars.

Weights were correlated by measuring again. Fortunately,

the weights were well distributed and each ~~deposited~~ far apart from another.

15
Student's Name

Date

Subject

Instructor's Name

EXPT. 3: Irrad. / 175°C / N_2 atm / NO follow-up H/T / VIALS

FUHT

Samples :- Barstok (from surface) \rightarrow constant radius.
Samples have 2.5 to 3 cm radii

4 samples \rightarrow 2.5, 10, 20, 50 Mrad

Method :- Thin strips in vials.

Vial filled with N_2 as in heat treatments.

Heater used this was small enough to fit under generator outlet

(heater provided by Prof Merrill)

cooling in air (room temp.)

vial will
Sample left in N_2 atmosphere at RT after irradiation
for >5 days

Analysis

Student's Name

10

Subject

Instructor's Name

EXPT 4: Imd / (75C / Air) / NO. FUHT / VIAL

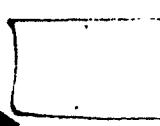
Samples : Bar Stock (b/w 2.5 to 3 cm radial distance)

4 Samples \rightarrow 2.5, ~~2.5~~, ~~2.5~~, 50 M Rad.



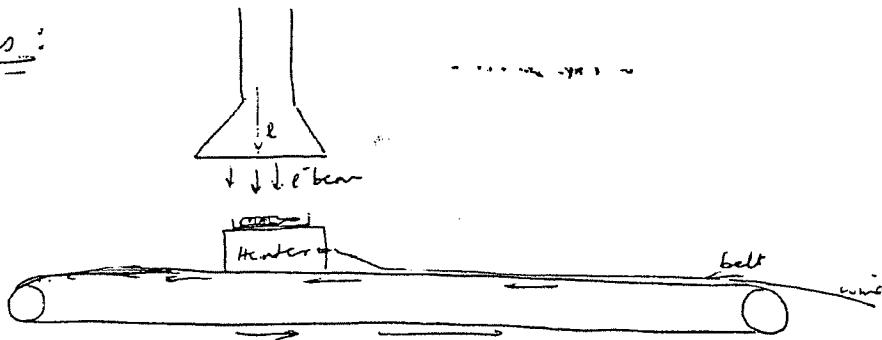
Method : (As in previous page)

Analysis



: E.T9X3

Apparatus:



Student's Name

Date

10

Subject

Instructor's Name

EXPTS: Irrad / RT / N₂ / NO-FU+T / VAC

Samples → Same as last page.

Method → Same as last page.

Done

①	2.5	Mrad
②	3.8	"
③	13.18	"
④	50	"

EXHIBIT - 4

E-IRRADIATION OF
THE MELT.

E-IRRADIATION OF THE MELT

Procedural Details:

The following experiment was performed at HVRL, MIT. The points to be noted ~~steps~~ were as follows:

- (1) Since the hot plate would not fit under the Van de Graaf generator, the specimens ^{in DSC pans} were placed in between two petridishes and laid on a metal plate acting as a heat sink while heating ~~to~~ (supplies heat when placed on the belt).
- (2) The heating was done at intervals ~~between~~ 100 °C - - - - -

- Start
- After 1.0 MRad
- " 2.5 MRad
- " 5.0 MRad
- " 10.0 MRad
- " 20.0 MRad
- " 30.0 MRad
- After 40.0 MRad

- (3) It can be assumed that approximately the temperature of the specimen was between 150 - 200 °C

NOTE:

- ① Absence of bimodal distribution during crystallization
 - because no crystals during irradiation,
 - One phase
 - (Scission & X-linking is defining in crystallization regions)
- ② Since ~~scission~~ lamellar size and crystallinity & Tm decreases,
i. significant crosslinking occurring
in proportion to scission.
If too much scission compared to crosslinking
 - mol wt would decrease
 - crystallinity & crystal size will increase
- (e) H) PE → 6.0%

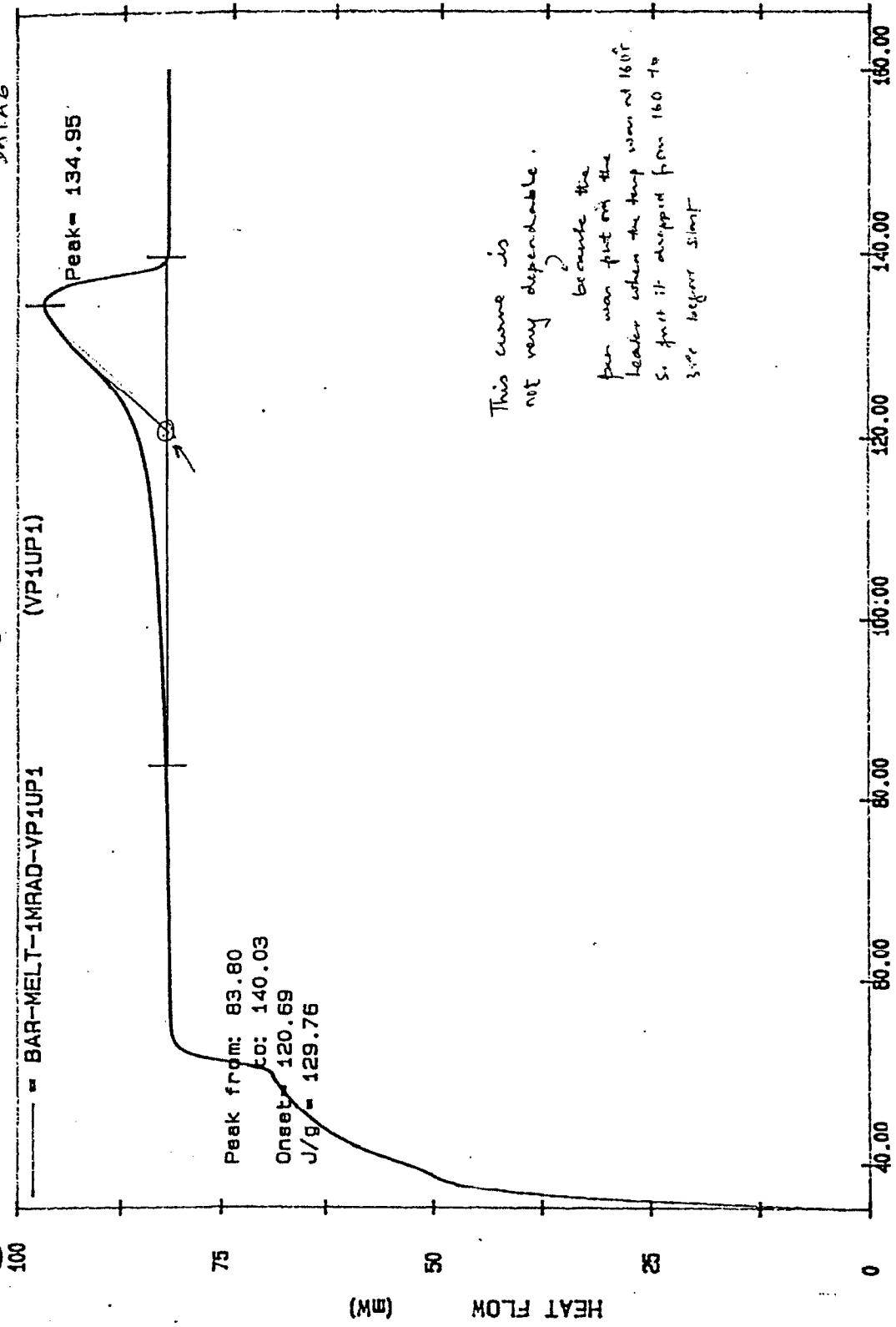
DATA 6

Method	Time (min)	Crystallization rate (10^{-6})	Avg. lamella thickness (nm)	Cryst. diff.	Remark.
1	10	12 ² 03	120 ² 22	1.08	-3.38
2.5	11	12 ² 96	118 ² 51	1.05	-2.26
5	11.6	12 ¹ 14	119 ¹ 32	1.07	-1.90
10	10.9	118 ⁰ 95	113 ⁰ 68	1.01	2.56
20	9.5	115 ⁰ 6	111 ⁰ 5	0.957	-1.31
50	9.6	105 ⁰ 50	101 ⁰ 18	0.948	-1.11

④ *Yunnanella* is drawn below 40% *for the first time*.

- ① Originating in the mesentery, it may spread to the liver, lungs, and other organs.
- ② Sudden drop in T_{core} (as in septicemia) after solid P_o (Bith, Tru, & Tru.)
- ③ People complain about decreasing an oral. chills increased (Bith, Frank, & Frank)
- ④ Originated from either \rightarrow 55%
- ⑤ Sustained, mild & steadily \rightarrow 30-45%

1. *Leucospermum* *cordifolium* *DC.*



Date: 3: 38pm
Scan: 10.0 C/min
Sample Wt: 9.732 mg Path: C:\PE\PEAKIN-ELMER DSC7
File #: VP1UP1 PREM1

Date 4

Page	Copy Off
122.0	1.15
122.0	21.30
122.0	21.48
122.0	0.24
122.1	21.09
122.1	-0.34
122.2	0.45
122.2	21.45
122.3	1.01
122.4	3.13
122.4	-0.44
122.5	-1.31
122.5	2.22
122.5	1.87
122.6	2.07
122.6	2.66
122.7	
122.8	18.89
122.8	0.12
122.8	1.12
122.9	4.10
122.9	-1.48
122.9	
122.9	-1.60
122.9	-0.02
122.9	1.02
122.9	-7.18
122.9	4.74
122.9	-0.77
122.9	-1.34
122.9	-0.50
122.9	8.88
123.0	8.72
123.0	12.24
123.0	
123.0	-0.74
123.1	9.10
123.1	2.78
123.1	6.75
123.2	13.23
123.2	13.00
123.3	-5.52
123.3	-7.78
123.4	-1.10
123.4	2.48
123.5	-1.31
123.5	-1.11

BAR-MELT-1MRAAD-VP1DN1

(VP1DN1)

Peak from: 96.35
to: 126.98
Onset= 123.93
J/g =-107.30

22.5
15
7.5
0
HEAT FLOW (mW)

180.00
160.00
140.00
120.00
100.00
80.00
60.00
40.00
0
Peak= 120.27
Shoulder
x. t. b. /

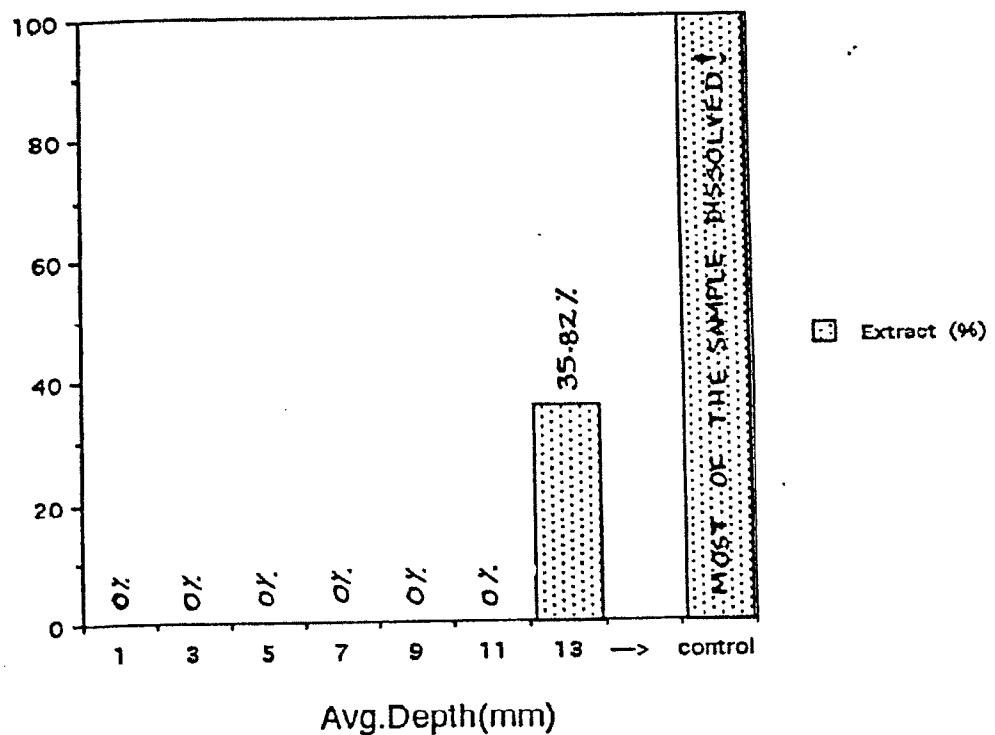
Date: 3/5/98
Scanning Rate: -10.0 C/min
Sample Wt: 9.732 mg Path: C:\PE\
File #: VP1DN1 PRENT

Temperature (C)

PERKIN-ELMER DSC7

EXHIBIT - 5

Extract percent in Decalin at 150 C (Samples from axis of irradiated cup 3)



Results from swelling test in Decalin at 150 C (Samples from axis of irradiated cup 3)

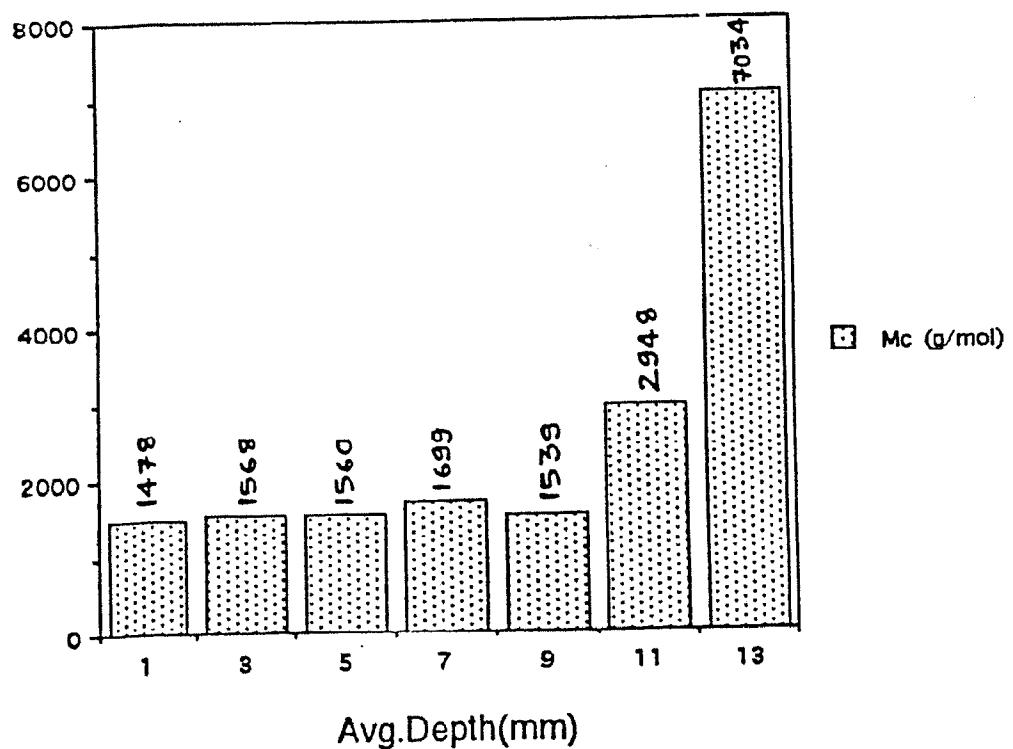
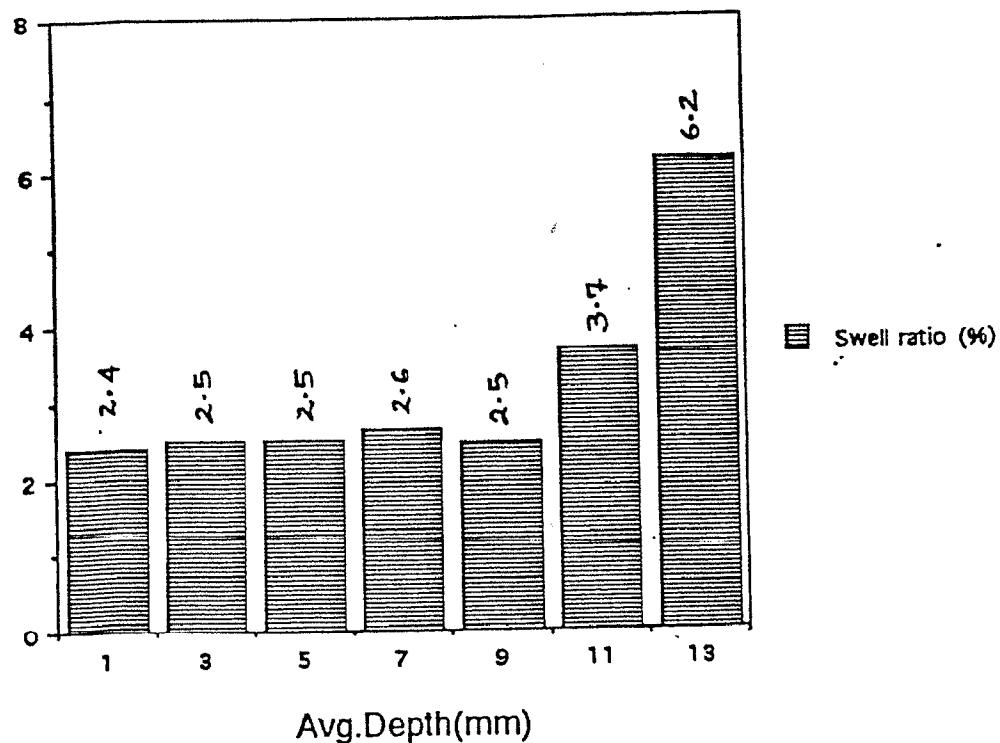
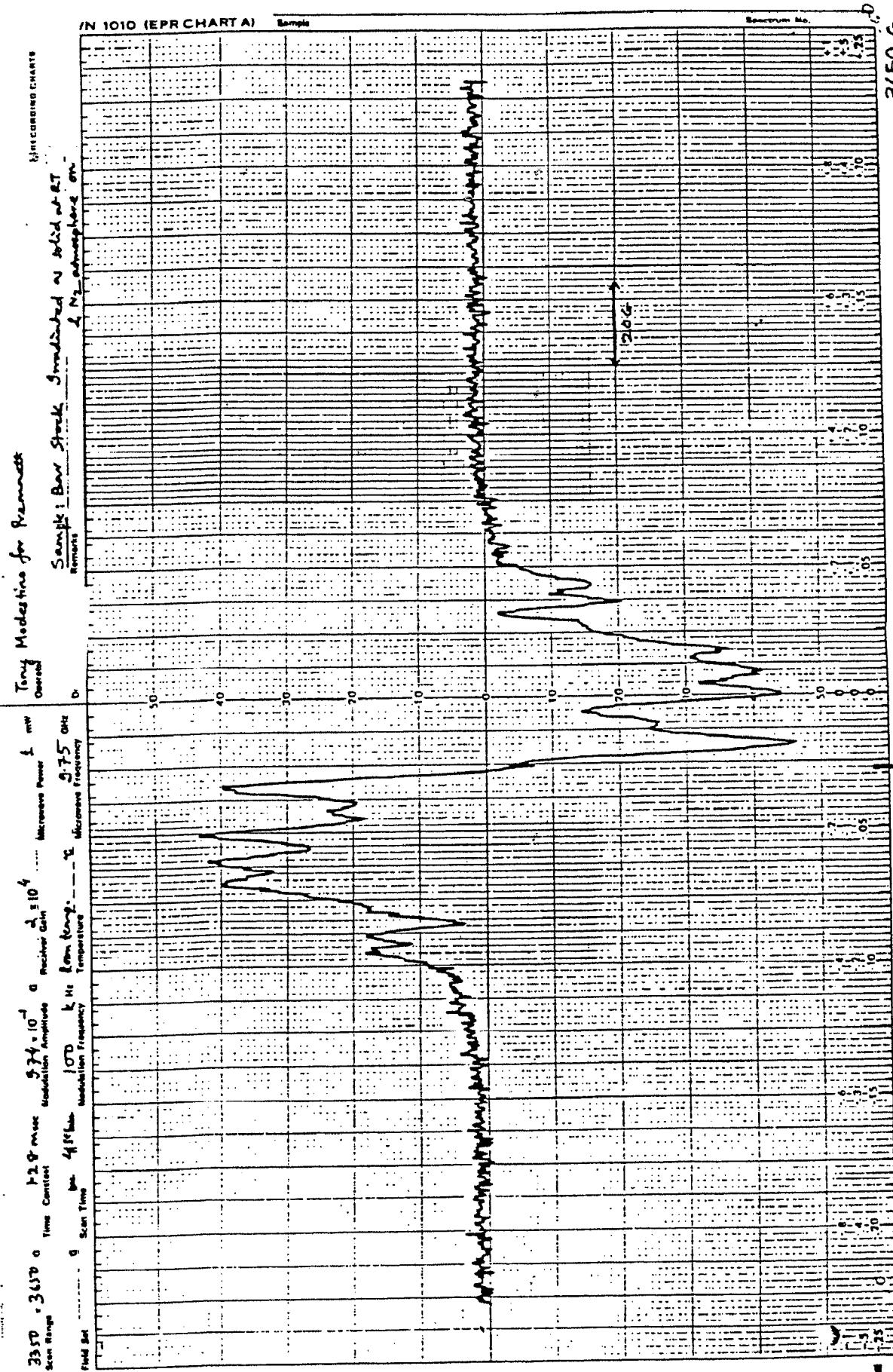


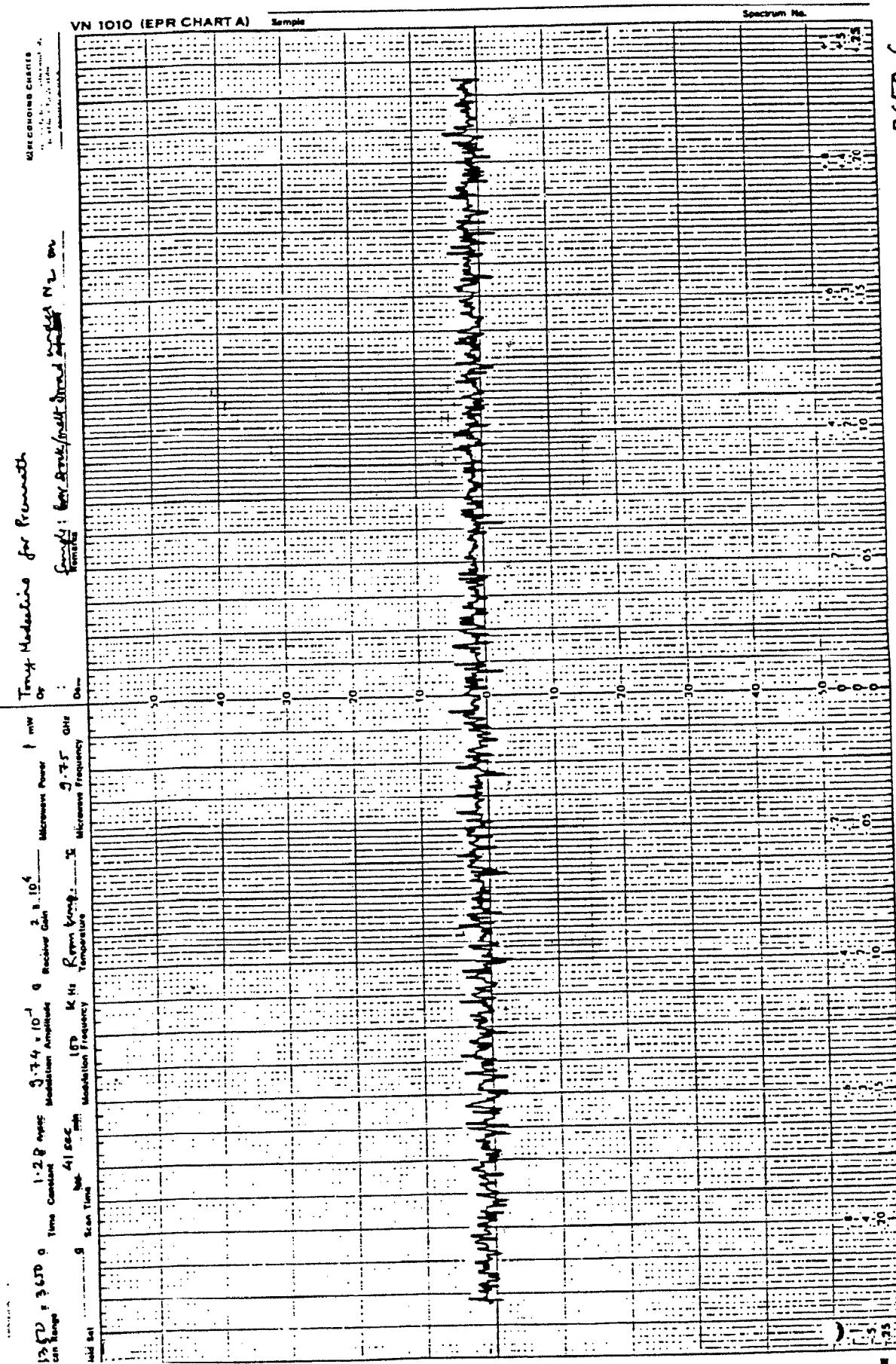
EXHIBIT - 6



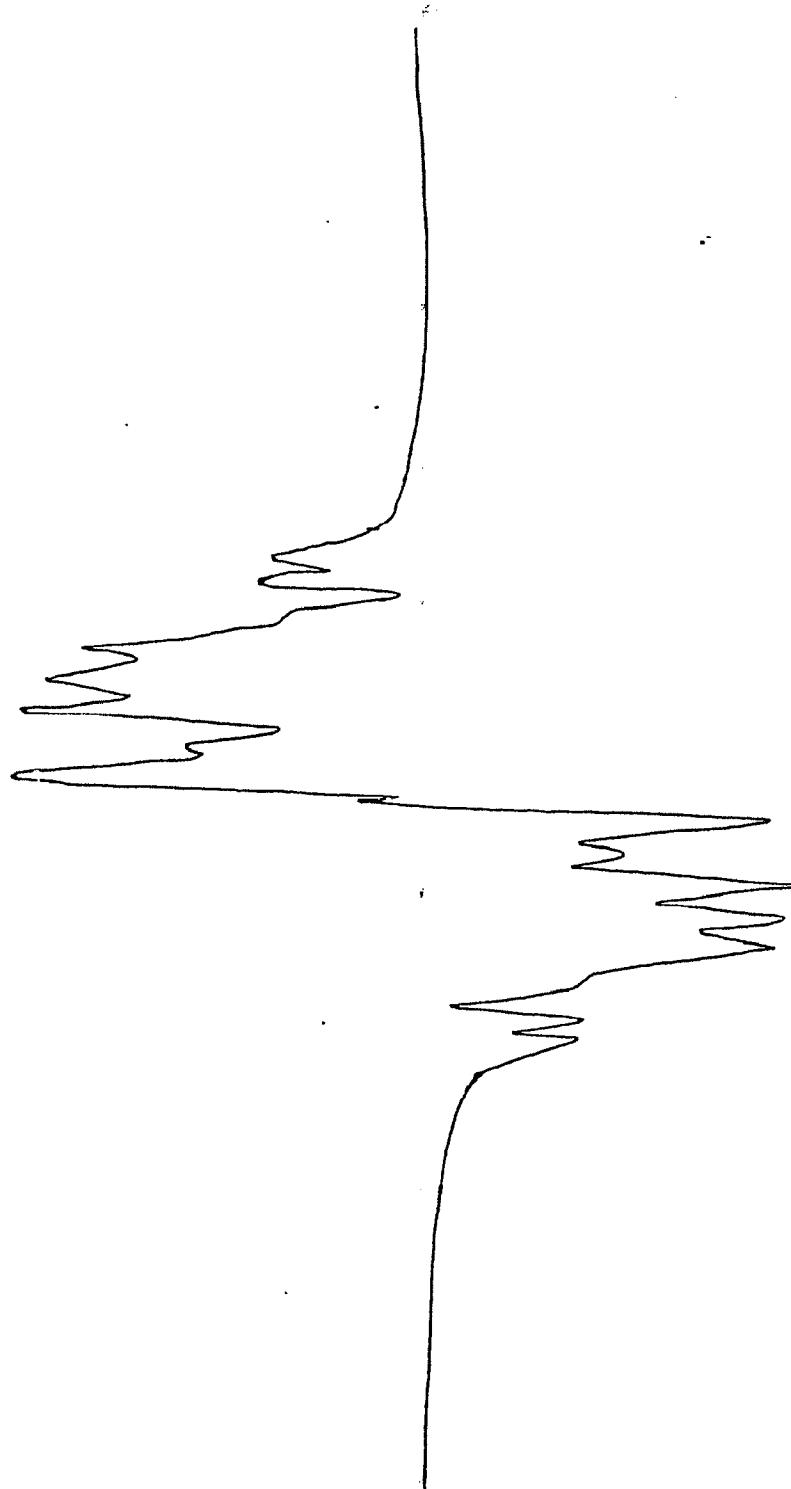
3480.43G
= 19.5G

5350 G

١٦



MIRROR IMAGE OF ESR SPECTRUM OF UHMWPE IRRADIATED AT RT / N₂ ATM.



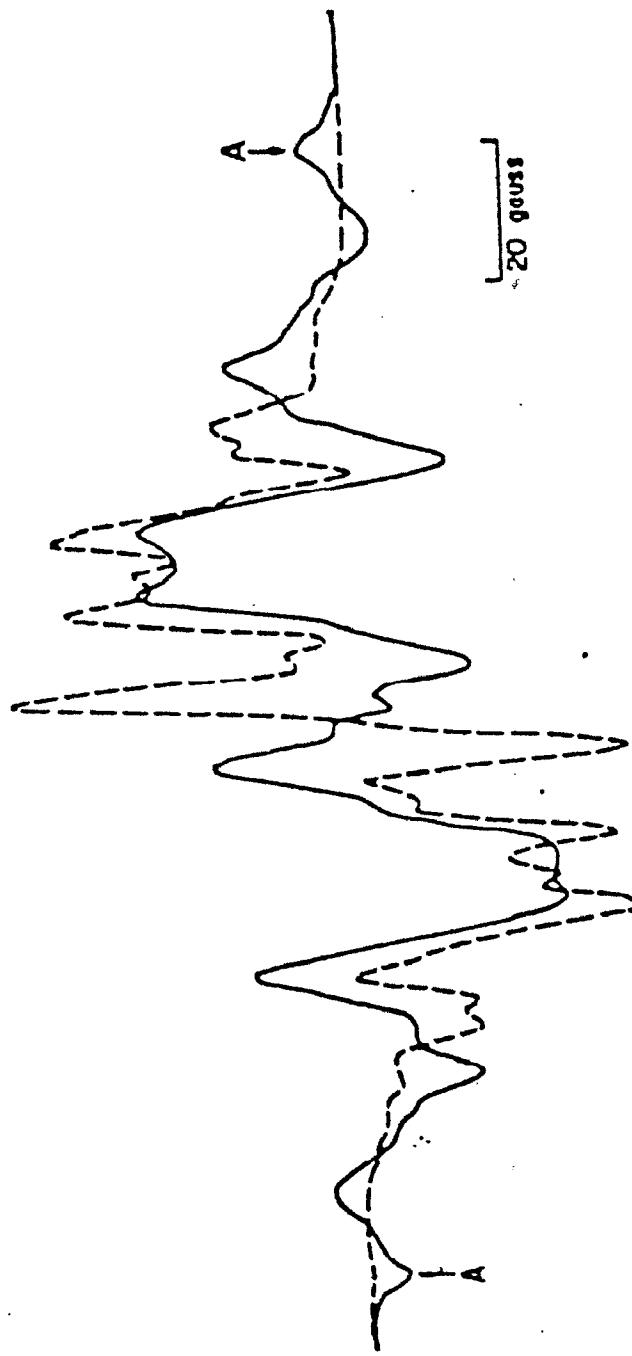


Figure 2. ESR spectra of allyl free radicals (dotted curve) and of mixed allyl and allyl free radicals after heating to room temperature (solid curve). Decay of allyl free radicals was calculated from height of peaks marked A.

REFERENCE : D.C. WATKINSON AND M. DOLE, J. Phys. Chem., 74 (9), 1970, 1913-1922